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16. ABSTRACT

EPA established drinking water regulations for ten inorganic substances and radionuclides that became effective on June 24, 1977. As a result of these new regulations, many communities may be required to construct new treatment facilities or to modify existing ones. This paper on arsenic and selenium is a second of a series that reviews existing treatment technology for meeting the EPA drinking water regulations. The effectiveness of conventional coagulation, lime softening, ion exchange, activated carbon reverse osmosis, and electrodialysis for the removal of the contaminants are discussed. The information consists of data from a general literature review and EPA's recent work on metals removal by conventional treatment.

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Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2

EPA-600/J-78-030
JOURNAL ARTICLE

Thomas J. Sorg and Gary S. Logsdon

This second article of a series outlines specific treatment technology for arsenic and selenium removal from potable water. The first article, which appeared in the February 1978 issue of the JOURNAL, discussed fluoride and nitrate removal. Subsequent articles will review the treatment technology for the six other NIPDWR-regulated inorganic contaminants and the radionuclides.

The EPA National Interim Primary Drinking Water Regulations (NIPDWR) established maximum contaminant levels (MCL) for ten inorganic contaminants. A set of regulations for radionuclides took effect at the same time, Jun. 24, 1977. Communities discovering that their water does not meet the regulations may have to consider water treatment to remove contaminants or lower contaminant levels.

The first article of this series discussed the treatment technology for removal of nitrates and fluorides. In this article, removal methods for arsenic and selenium are outlined. Because of the general lack of data on removal of inorganic substances from water, much of the information presented here is drawn from the research efforts of the Water Supply Research Div., USEPA, Cincinnati, Ohio. The basic philosophy of that program is first to evaluate the effectiveness of conventional coagulation and lime softening processes. If they are found to be ineffective, ion exchange and reverse osmosis are studied. The research is divided into two phases—laboratory jar tests and pilot-plant tests to verify laboratory results.

Arsenic Removal From Water

Health effects. Of the ten inorganic contaminants listed in the National Interim Primary Drinking Water Regulations (NIPDWR), arsenic (0.05 mg/l MCL) is certainly most well-known by the average person as a hazard to human health. Although some organic forms have been used for medical treatment, arsenic is not known to be an essential element for humans. Arsenic can occur in four oxidation states in water, but generally is found in only the trivalent and pentavalent states. The element forms both inorganic and organic compounds; the inorganic compounds are more toxic than the organic compounds, and the trivalent form is more toxic than the pentavalent form. The toxicity is also dependent on the chemical form, and the route, duration, and rate of arsenic exposure.[1]

No adverse health effects have been reported from the ingestion of water containing arsenic levels of 0.1 mg/l,[1] but chronic or subacute toxicity has been observed with the ingestion of a few milligrams per day for two weeks or longer.[2] The initial symptoms reported are skin erythrema, edema, and pigmentation, and gastrointestinal and neurological disturbances. Other conditions reported to be caused by high levels of arsenic are neuropathy, increased heart attacks, and vascular injury leading to gangrene and "black foot disease."[1,2]

Arsenic is believed to be a potential carcinogen, with inorganic arsenic compounds linked to the development of cancer of the skin, respiratory system, and the gastrointestinal tract. Because animal studies have not shown arsenic compounds to be carcinogenic, doubt still exists on whether it is a human carcinogen. The National Academy of Science (NAS) report on the NIPDWR[3] concluded that "the absence of positive results from controlled animal studies makes it impossible to estimate quantitatively a risk of cancer from intake of arsenic in any form or concentration."

JAWWA, 379-393, July 1978

The same report speculated that interactions between arsenic and heavy metals or irritating substances significantly affect humans exposed to mixtures of these contaminants. For example, although arsenic protects against selenium poisoning in some circumstances, the two appear to be additive in toxicity. Because of the general lack of information in this area, the NAS has recommended investigations on the interaction of arsenic with other trace elements in the environment.[2]

The maximum no-observed-adverse-effect for arsenic in water is less than 100 μg/l. The intake from 2 l of water per day containing 20 μg/l is therefore slightly greater than ten per cent of the median total intake, reported to be 137–300 μg/l, from all sources in the US. From these basic assumptions, the NAS concludes that the "current mandatory US drinking water limit of 50 μg/l provides a meager margin of safety." Although the NAS does not specifically recommend that the existing 0.05-mg/l limit for arsenic be lower, it definitely does not support raising the MCL.

The 1969 Community Water Supply Study[3] on 969 water utilities reported that finished water from less than 1 per cent of the utilities exceeded the 0.05-mg/l limit. Although this study indicated that arsenic was not a serious problem in finished waters, other information suggests otherwise. In 1970, Kopp and Kroner[4] reported that 7 per cent of 1500 water samples collected from 150 rivers in the US contained arsenic. A year later, Durum et al[5] found 21 per cent of 727 samples from rivers and lakes contained arsenic.

Because arsenic is a common mineral in many western states, it is probably present in many groundwater supplies serving small communities. Because the Western States Agencies have many small community water supplies to sample, the magnitude of the arsenic problem will not be determined for several years.

Arsenic chemistry overview. Arsenic can occur in aquatic systems in four oxidation states; however, it is normally found as an anion with acid characteristics in only the trivalent (arsenite) and pentavalent (arsenate) forms. In natural waters, the valence and the species are dependent on oxidation-reduction conditions and the pH of the water. In a system including oxygen and sulfur, Ferguson and Gavis[6] showed that the soluble arsenite species are H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{-2}$. The soluble arsenate species are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$, and AsO_4^{-3}. In the pH range 4–10, the predominant arsenite form is H_3AsO_3 and the predominant arsenate species are $H_2AsO_4^-$ and $HAsO_4^{-2}$. The rate of oxidation of arsenic III to arsenic V with oxygen was found to be very slow at neutral pH values, but proceeds measurably in several days in strong alkaline or acid solutions.[6]

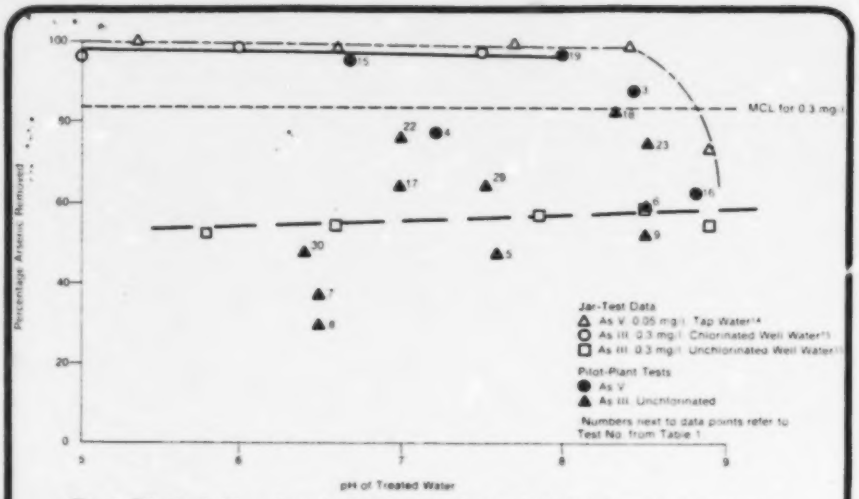
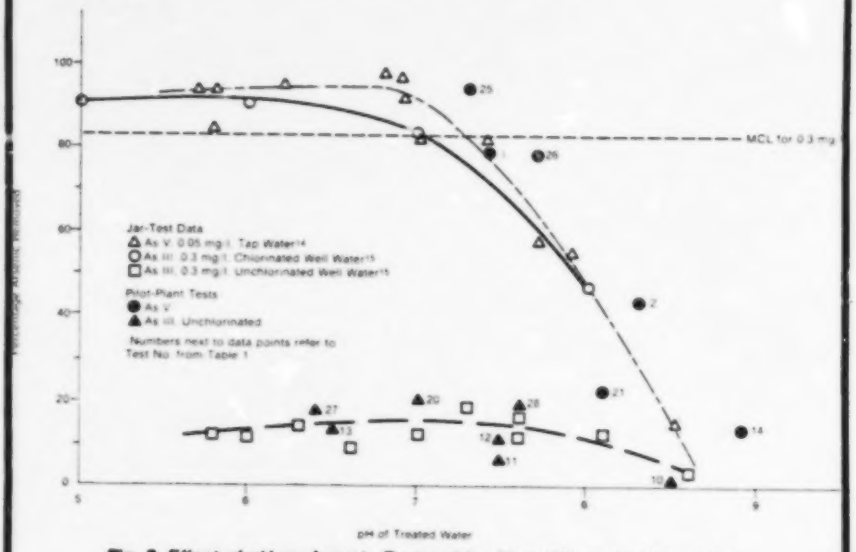

Percentage Arsenic Removed
pH of Treated Water
MCL for 0.3 mg/l
Jar-Test Data
As V, 0.05 mg/l, Tap Water[14]
As III, 0.3 mg/l, Chlorinated Well Water[15]
As III, 0.3 mg/l, Unchlorinated Well Water[15]
Pilot-Plant Tests
As V
As III, Unchlorinated
Numbers next to data points refer to Test No. from Table 1

Fig. 1. Effect of pH on Arsenic Removal by Ferric Sulfate (30 mg/l) Coagulation


Percentage Arsenic Removed
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As III, 0.3 mg/l, Unchlorinated Well Water[15]
Pilot-Plant Tests
As V
As III, Unchlorinated
Numbers next to data points refer to Test No. from Table 1

Fig. 2. Effect of pH on Arsenic Removal by Alum (30 mg/l) Coagulation

Based upon a general review of the literature, arsenite is more likely to be found in anaerobic groundwaters and arsenate in aerobic surface waters. Because information on conventional coagulation and lime softening treatment shows that arsenic removal is valence dependent, steps should be taken to identify the arsenic form causing an arsenic problem before evaluating possible solutions.

Very little work has been done to identify the specific forms of arsenic found in drinking water supplies because the commonly used analytical techniques such as atomic absorption do not distinguish between valence states. During fiscal year 1977, EPA awarded a research grant to Texas A&M Univ. to develop a reliable arsenic speciation analytical technique. Problems of sample preservation resulted in the project's being expanded to develop suitable methods of arsenic sample preservation. Progress reports have indicated that neither task has a simple solution.

Geochemistry and chemistry investigations on the removal of arsenic from solution indicate that arsenate should be easier to remove from water than arsenite by conventional coagulation treatment. LaPeintre[7] showed that arsenate species coprecipitate with, or adsorb onto, hydrous iron oxides; Orish and Sandell[8] reported that arsenate can also be adsorbed by aluminum hydroxide and clays. Studies on arsenite, on the other hand, indicate that it may not be easily removed. Mackenthun's measure-

TABLE 1
Results of Conventional Coagulation Pilot-Plant Tests for Arsenic Removal

Test No.	Date Started	Length of Test hr	Test Water	Coagulant		pH of Treated Water	Arsenic Contaminant		Percentage Arsenic Removed				
										Filtered Water			
											Granular Activated Carbon Filters		
				Type	Dose mg/l		Form	Raw Water Concentration mg/l	Settled Water	Dual-Media Filter	Virgin GAC*	Exhausted GAC*	Virgin GAC†
1	11/11/74	101	Cincinnati tap	alum	26	7.4	As V	0.41	56	79	–	–	–
2	11/18/74	102	Cincinnati tap	alum	26	8.3	As V	0.39	31	44	–	–	–
3	12/9/74	102	Cincinnati tap	ferric sulfate	19	8.4	As V	0.50	75	89	–	–	–
4	12/16/74	102	Cincinnati tap	ferric sulfate	15	7.2	As V	0.30	46	78	–	–	–
5	4/28/75	98	gravel pit	ferric sulfate	19	7.6	As III	0.43	25	47	–	–	–
6	5/5/75	99	gravel pit	ferric sulfate	18	8.5	As III	0.48	38	58	–	–	–
7	5/12/75	99	gravel pit	ferric sulfate	18	8.5	As III	0.45	20	36	–	–	–
8	5/19/75	100	gravel pit	ferric sulfate	15	8.5	As III	0.25	6	29	–	–	–
9	5/26/75	99	gravel pit	ferric sulfate	15	8.5	As III	0.27	27	52	–	–	–
10	6/2/75	100	gravel pit	alum	27	8.5	As III	0.39	1	1	–	–	–
11	6/9/75	102	gravel pit	alum	20	7.5	As III	0.47	3	6	–	–	–
12	6/16/75	100	gravel pit	alum	17	7.5	As III	0.54	9	11	–	–	–
13	6/23/75	100	gravel pit	alum	15	8.5	As III	0.46	8	13	–	–	–
14	11/10/75	95	Ohio River	alum	24	8.9	As V	0.37	14	14	11	–	–
15	11/17/75	100	Ohio River	ferric sulfate	25	6.7	As V	0.39	81	96	98	–	–
16	12/1/75	98	Ohio River	ferric sulfate	28	6.8	As V	0.33	46	62	61	–	–
17	8/30/76	100	Ohio River	ferric sulfate	29	7.0	As III	0.12	36	64	90	91	–
18	9/20/76	92	Ohio River	ferric sulfate	28	8.3	As III	0.12	61	82	80	81	–
19	1/17/77	92	Ohio River	ferric sulfate	30	8.0	As V	0.26	80	95	97	95	–
20	5/23/77	93	Ohio River	alum	29	7.0	As III	0.16	14	21	–	35	44
21	7/11/77	95	Ohio River	alum	27	8.1	As V	0.17	17	23	–	37	24
22	8/8/77	89	Ohio River	ferrous sulfate	33	7.0	As III	0.23	40	76	–	83	84
23	8/15/77	91	Ohio River	ferrous sulfate	28	8.5	As III	0.20	52	73	–	68	84
24	8/29/77	90	Ohio River	ferrous sulfate	30	8.6	As V	0.81	62	76	–	75	76
25	10/31/77	88	Ohio River	alum	25	7.3	As V	0.16	74	95	–	96	94
26	11/7/77	91	Ohio River	alum	27	7.7	As V	0.22	71	79	–	82	83
27	11/14/77	92	Ohio River	alum	40	6.4	As III	0.62	18	18	–	29	36
28	1/6/78	76	well water	alum	28	7.6	As III	0.21	10	19	–	27	29
29	2/6/78	70	well water	ferric sulfate	33	7.5	As III	0.22	48	62	–	72	67
30	2/13/78	90	well water	ferric sulfate	30	6.4	As III	0.19	30	47	–	71	58

*Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
†Hydrodarco 1000, ICI United States, Inc., Wilmington, Del.

ments[9] of arsenic concentrations in sodium arsenite-treated lakes showed that removal of arsenic from solution and its accumulation in sediments occurred only occasionally. Frear[10] and Gilderhus[11] also reported little removal of sodium arsenite from arsenic-rich soils or sediments. Based upon the results of these studies, conventional coagulation treatment should be more effective for arsenate removal than for arsenite removal.

Treatment methods. The only treatment methods that have been thoroughly studied for arsenic removal are conventional coagulation and lime softening. Very few investigations have studied the use of ion exchange, powdered or granular activated carbon, reverse osmosis, or electrodialysis.

Conventional coagulation. Investigations on arsenic removal from water by conventional coagulation treatment began as early as 1934, with work by Buswell et al,[12] and more recently by Shen,[13] Gulledge and O'Connor,[14] and Logsdon et al.[15] All of these investigations indicate that the removal of arsenic by coagulation treatment is a function of the oxidation state of the arsenic, the type and dose of coagulant, the pH of the treated water, and the initial arsenic concentration.

In the early studies of Buswell et al[12] jar and pilot-plant tests were conducted on water spiked with large amounts of sodium arsenate (As V) and sodium arsenite (As III). Ferric sulfate and alum were used as coagulants. Ferric sulfate was found to be more effective than alum, and arsenic III removals similar to arsenic V removals could be achieved by first oxidizing the arsenic III to V with calcium hypochlorite. For example, in pilot-plant tests a 25-mg/l concentration of arsenic V could be reduced to 5 mg/l with 136 mg/l of ferric sulfate. With oxidized arsenic III, the same dose of ferric sulfate was slightly less effective; arsenic III concentration was reduced from 25 mg/l to about 7 mg/l.

More recent investigations used jar-test studies with water spiked with arsenic concentrations of 0.05 to 10.0 mg/l. Gulledge and O'Connor[14] studied the effect of the type and dose of coagulant and of pH on the removal of 0.05 mg/l of arsenic V. Logsdon et al[15] investigated the effect of type and dose of coagulant, pH, and the initial arsenic concentration on removal of both arsenic III and V from well water.

The effects of pH and coagulant on

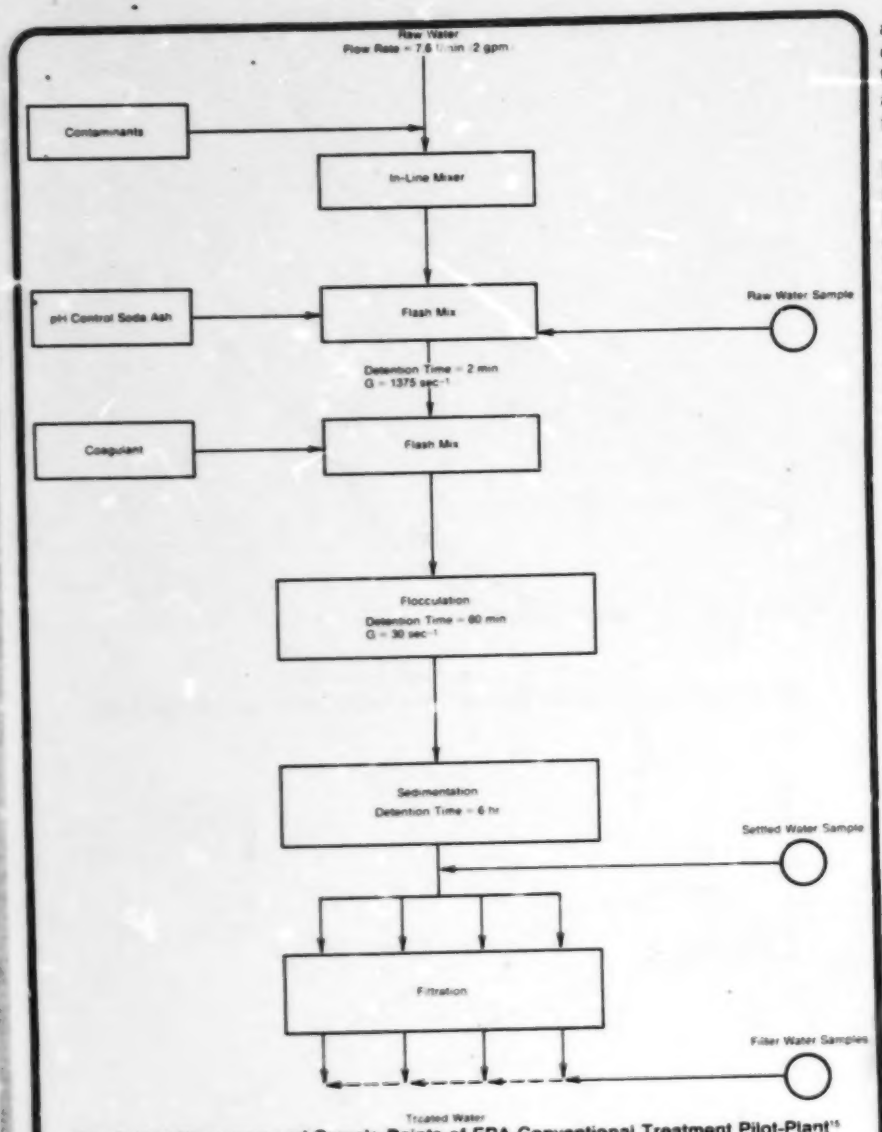


Fig. 6. Unit Processes and Sample Points of EPA Conventional Treatment Pilot-Plant[15]

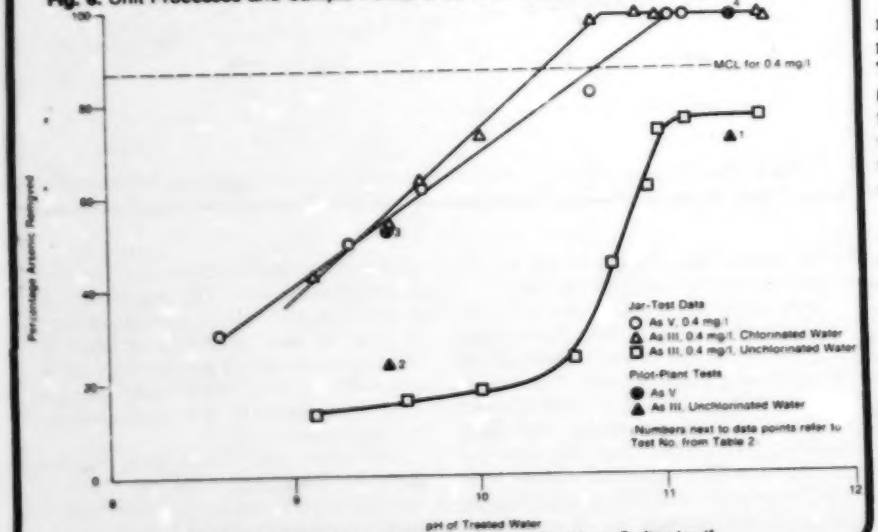

MCL for 0.4 mg/l
Percentage Arsenic Removed
pH of Treated Water
Jar-Test Data
As V, 0.4 mg/l
As III, 0.4 mg/l, Chlorinated Water
As III, 0.4 mg/l, Unchlorinated Water
Pilot-Plant Tests
As V
As III, Unchlorinated Water
Numbers next to data points refer to Test No. from Table 2.

Fig. 7. Effect of pH on Arsenic Removal by Lime Softening[15]

achieved with arsenic III concentrations of 0.8 mg/l or lower. With preoxidation, the MCL is attainable with 30 mg/l of alum when the arsenic III concentration is less than 0.2 mg/l.

If the arsenic MCL (0.05 mg/l) cannot be achieved with coagulant doses of 30 mg/l, removals can be improved by increasing the coagulant dose. Figures 3, 4, and 5 show the results of studies of Logsdon et al on determining the effect of increased coagulant dose on arsenic III and arsenic V removal. In the optimum pH range of 5.7–8.0, ferric sulfate can achieve greater increases in removals than alum at the same incremental dosage increase. The three figures also reveal that the benefits derived by increasing the dose are greater with higher turbidity river water than with low turbidity well water, indicating that turbidity may also affect removals.

In addition to the jar-test studies done by Logsdon et al at the Water Supply Research Division (WSRD), EPA, Cincinnati, Ohio, the WSRD has done pilot-plant studies on arsenic removal. The pilot-plant system used for the arsenic studies, and for other heavy metal studies to be discussed in this series, was originally constructed in 1974 at the EPA Taft Engrg. Ctr., Cincinnati, Ohio. In 1976, the plant was moved to the new EPA Envir. Res. Ctr. in the same city. During the reassembling phase, the plant was slightly modified to improve its flexibility and usefulness.

The WSRD pilot plant is capable of treating two parallel streams, each 7.6 l/m (2 gpm), of water. The parallel treatment trains were designed to be operated in a conventional manner, but with the flexibility to bypass any of the treatment steps and to be operated in series. A flow diagram and the pertinent design data of one of the treatment trains is shown in Fig. 6.

Each treatment train has two rapid-mix basins, a flocculation basin, a sedimentation tank and four parallel filters. The test water is pumped from a 28.4-m³ (7500-gal.) stainless steel storage tank to the first rapid mix tank. From here the water flows by gravity through coagulation, flocculation, and sedimentation steps to the filter columns.

The filtration rate of the filters is controlled by pumps on the effluent side of each filter. Although the system can employ four parallel filters, each with a diameter of 10.8 cm (4.25 in.), at a loading rate of 2.5×10^{-3} m/s (4 gpm/sq ft), the actual number used varied from one to four. The filter materials were changed periodically and the following different filter media were used:

1. Dual-media—51-cm (20-in.) anthracite* with an effective size (ES) of 1.2 and

*Anthrafilt, Shamokin Filter Co., Shamokin, Pa.

uniformity coefficient (UC) of 1.5 over 30 cm (12 in.) of sand* with an ES of 0.4 and UC of 1.7
2. GAC†—76 cm (30 in.)
3. GAC‡—75 cm (30 in.)
4. Exhausted GAC§—76 cm (30 in.)
5. GAC§—76 cm (30 in.)

The test waters for the pilot-plant studies were Cincinnati tap water; Ohio river water; Glendale, Ohio, well water; and a low-turbidity, gravel-pit water from the Cincinnati area. Except for Cincinnati tap water, all test waters were trucked to the plant on an as-needed basis in a 19-m^3 (5000-gal) tank trailer.

A normal pilot-plant test ran 90–100 hours of continuous treatment from Monday morning to Friday afternoon. Because none of the test waters contained arsenic, they were spiked with either sodium arsenite or sodium arsenate. One-litre grab samples of the raw, settled, and filtered water were normally collected at 12-hour intervals. Samples were preserved with concentrated nitric acid and analyzed for arsenic by atomic absorption spectrophotometer methods. A summary of the arsenic removal results is given in Table 1. Each removal percentage is an average of 8–10 grab samples.

The dual-media filter results are plotted in Fig. 1 and 2 for comparison with jar-test results. Although the test conditions and waters were not always identical, the pilot-plant removal results generally agreed with jar-test results. They confirmed that (1) arsenic V is more effectively removed than arsenic III by alum and ferric sulfate coagulation; (2) ferric sulfate coagulation achieves higher arsenic III removals than alum; and (3) removals of arsenic V by alum coagulation are very dependent on the pH of the treated water. No pilot-plant studies were conducted on the removal of oxidized arsenic III.

The significance of the oxidation state and the type of coagulant on arsenic removal was also shown in an investigation by Shen[13] on Taiwan groundwater containing naturally occurring arsenic. Shen's initial laboratory studies determined the effect of plain sedimentation, coagulants, oxidation and coagulation, and filtration; the laboratory tests were then repeated on a pilot-plant scale.

Shen's sedimentation experiments showed some arsenic removal by settling, but sedimentation was ineffective and time consuming. For example, after one full day of settling, the arsenic concentration was reduced only from 0.8 mg/l to 0.73 mg/l, or 8.7 per cent removal. At the end of 15 days, the settled water contained 0.41 mg/l of arsenic for a total removal of only 49 per cent.

Shen tested three coagulants for arsenic removal: ferrous sulfate, ferric chloride, and alum. The highest removals (82 per cent) were achieved with ferric chloride. Alum produced 32 per cent removal and ferrous sulfate only 24 per cent. Shen therefore concluded that the removal process was of a chemical nature with iron hydroxide rather than a process of physical adsorption.

Shen did not identify the oxidation state of the arsenic in the well water used in his experiments. The oxidation and coagulation test results indicate, however, that it was probably arsenic III, because removals of greater than 90 per cent with ferric chloride were achieved only when the water was oxidized prior to coagulation.

Oxidation and coagulation studies done by Shen with varying doses of potassium permanganate and chlorine as oxidizing agents indicated that chlorine was the better oxidizing agent, although

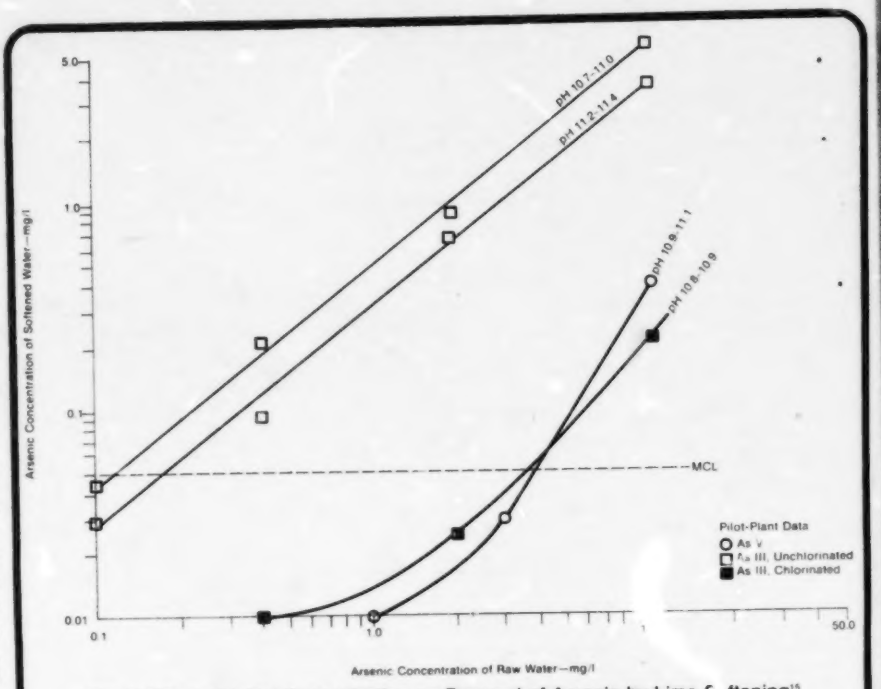


Fig. 8. Effect of Initial Concentration on Removal of Arsenic by Lime Softening[15]

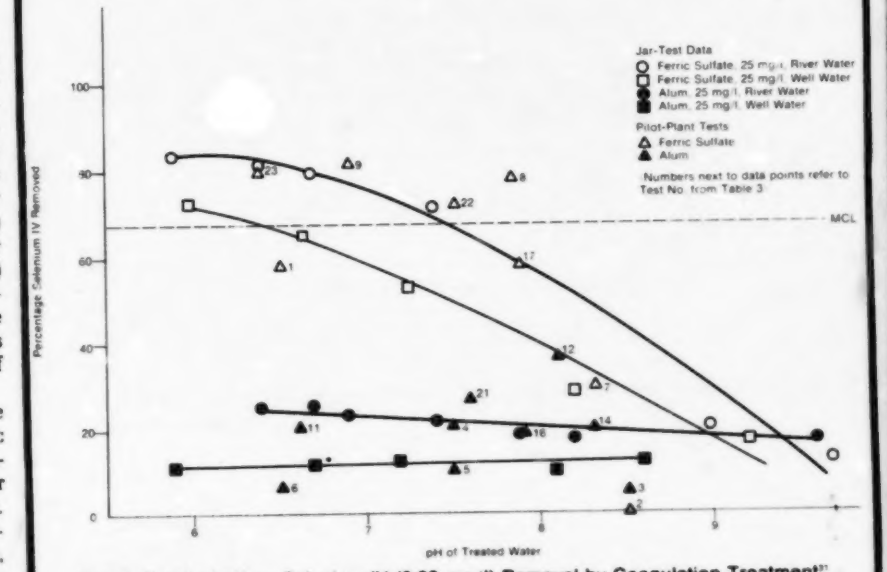
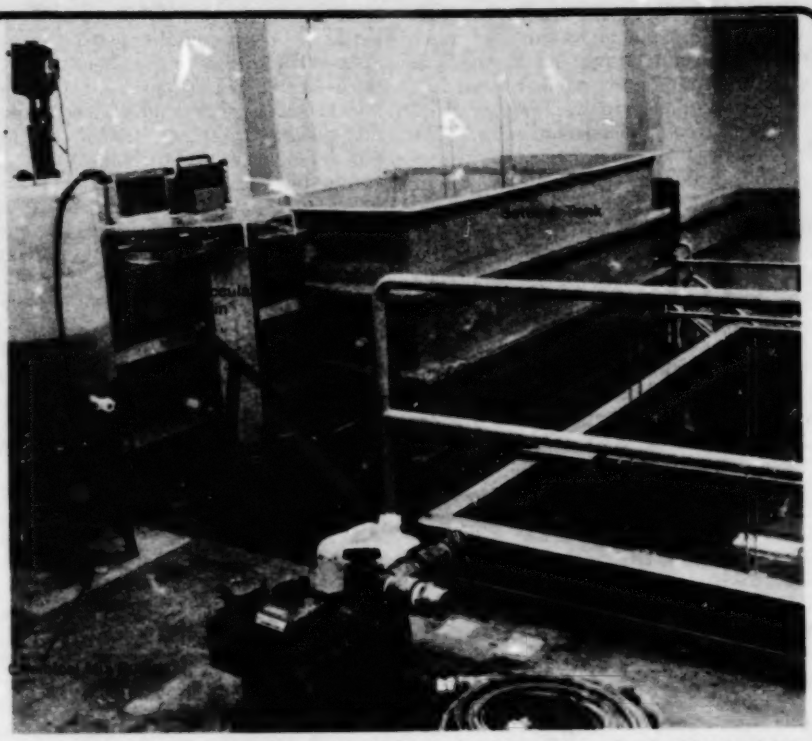
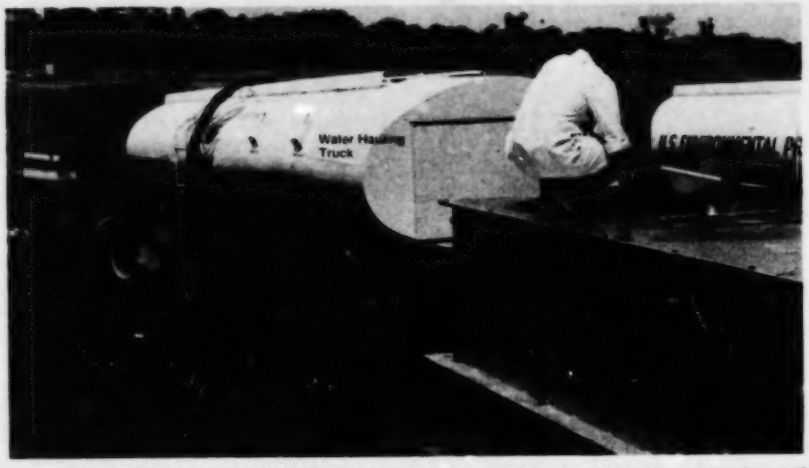

Percentage Selenium IV Removed
pH of Treated Water
Jar-Test Data
Ferric Sulfate, 25 mg/l, River Water
Ferric Sulfate, 25 mg/l, Well Water
Alum, 25 mg/l, River Water
Alum, 25 mg/l, Well Water
Pilot-Plant Tests
Ferric Sulfate
Alum
Numbers next to data points refer to Test No. from Table 3
MCL

Fig. 9. Effect of pH on Selenium IV (0.03 mg/l) Removal by Coagulation Treatment[27]

*Muscatine sand, Northern Gravel Co., Muscatine, Iowa
†Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
§Hydrodarco 1030, ICI United States Inc., Wilmington, Del.



The treatment facilities at the WSRD pilot plant consist of two trains, one of which is pictured here, each with chemical mix tanks, a flocculation basin, settling tank, and sedimentation tank.



Raw waters for testing at the WSRD pilot plant are hauled by truck to storage tanks at the facility.

both oxidants significantly increased iron coagulation removals. When Shen tried aeration alone and in combination with coagulation, he found that aeration had no apparent effect on arsenic removals, indicating that aeration cannot oxidize arsenite to arsenate in a short time. These results are consistent with the previously mentioned statements of Ferguson and Gavis[6] on the slow rate of oxidation of arsenite to arsenate with oxygen.

Following the completion of the pilot-plant studies, Shen concluded that the only treatment technique continuously capable of achieving high arsenic removal was ferric chloride coagulation preceded by chlorine oxidation and followed by sedimentation and filtration.

Based on Shen's laboratory and pilot-plant results, a full-scale arsenic removal plant was designed and constructed in Taiwan in 1969 to treat 150 m^3/day (0.04 mgd) to serve 1500 people. During the first 59 days of operation, when the raw water arsenic concentration was 0.6 to 0.94 mg/l, plant operation data showed arsenic removals from 82 to 100 per cent (below detectable limit). Because the plant was successful, Shen stated that the Taiwan government had decided to use this method of treatment for other arsenic-contaminated water supplies. Whether other plants have since been built is not known.

Lime softening. Arsenic can be removed very effectively from hard water by lime and excess lime softening treatment, with the amount of removal dependent upon the pH and the valence of the arsenic contaminant. Jar-test study results reported by Logsdon et al[15] showed that arsenic V was more readily removed from hard water than arsenic III and that removals of both forms increased with increasing pH. The results of these lime softening studies on well water having an initial hardness of around 300 mg/l as $CaCO_3$ are shown in Fig. 7. At pH 10.5 and above, almost 100 per cent removal was obtained on water spiked with 0.4 mg/l of arsenic V. The best removal of arsenic III was about 80 per cent at pH 11.1 and above. Below the optimum pH range, arsenic V and III removals decreased with decreasing pH, with arsenic V removals always higher than arsenic III removals.

As with conventional coagulation treatment, arsenic III removals almost identical to arsenic V removals can be achieved by oxidizing arsenic III to arsenic V prior to treatment. The results of jar-test studies on arsenic III removal done by Logsdon et al with chlorine oxidant are also plotted on Fig. 7 to show the similarity of two removal curves.

The capability of achieving the arsenic MCL by lime softening is dependent on the initial concentration and percentage of removal. Logsdon et al[15] studied the effect of initial concentration on arsenic V and III removal and the results are shown in Fig. 8. In the optimum pH range, the data indicate that the arsenic MCL can be achieved if the concentration of arsenic V or oxidized arsenic III in the raw water is 0.35 mg/l or lower. If arsenic III levels are less than 0.1 mg/l, Fig. 8 shows that preoxidation is not necessary to achieve the MCL, if softening is done at pH 10.7 or above.

The WSRD conducted several lime-softening pilot-plant studies on removing arsenic from well water using the system shown in Fig. 6. Two test runs were completed at pH 9.5 and 11.3 for each arsenic form. The pilot-plant system was operated in the same manner as conventional coagulation for softening at pH 9.5. At pH 11.3, modifications provided for recarbonation and additional settling; the settled water was pumped to the settling tank of the parallel treatment system, where the water was recarbonated to lower the pH to 9.6. The recarbonated water flowed through the sec-

ond settling tank before entering the filters. To determine if additional arsenic removal was achieved by recarbonation and additional settling, extra grab samples of the effluent water were collected from the second settling basin. The results of the four lime-softening pilot-plant test runs are listed in Table 2 and the dual-media filter removals are plotted on Fig. 7. The arsenic V removal results are identical to those achieved in the jar-test studies and the arsenic III removal results were comparable. No pilot-plant test runs were done with oxidized arsenic III.

Ion exchange. Very few ion exchange studies on the removal of arsenic from water have been reported in the literature. The limited data from these studies show, however, that arsenic can be removed with anion exchange resins but not with cation resins. Because arsenic occurs as an anion and cannot be removed with cation resins, neither the common household water softener nor the conventional zeolite softening system can remove arsenic from water.

The practicability of removing arsenic by anion ion exchange is questionable because the effect of competitive anions in the water is not known. The arsenic ion exchange studies reported in the literature were basically short screening tests to determine if arsenic could be removed by this treatment technique. None of the studies evaluated the effect of other anions on the efficiency of arsenic removal.

Calmon[16] reported the use of cation and anion exchangers for arsenic removal. The test waters were "field waters" samples containing 68 mg/l of arsenic V. Batch-type equilibrium tests with several different anion resins in the chlorine form showed removals of 55 to 82 per cent, the latter achieved with a weak base resin.* No removal was achieved with cation exchange resins.

Column tests conducted with the same weak base resin using HCl and NaOH as regenerants showed 100 per cent removals with the resin regenerated with HCl and 93 per cent with resin regenerated with NaOH. The recovery of arsenic was not complete with either regenerant—77 per cent with HCl and 73 per cent with NaOH. Calmon's studies were preliminary and did not include the effects of other variables.

Shen[13] ran several column tests with the same weak base resin used by Calmon. Only 20.7 per cent removal was obtained with synthetic water containing 1.06 mg/l of arsenic III. Tests with natural water containing 0.84 mg/l of naturally occurring arsenic resulted in 100 per cent removal. The differences in results were not explainable by Shen.

*Ionac A-260, Ionac Chemical Corp., Birmingham, N.J.

Bellack[17] accidentally discovered that activated alumina* and bone char could remove arsenic from water. Because arsenic sorption on bone char caused an irreversible change in the chemical structure of the char, Bellack concentrated his investigation on the use of activated alumina. Column studies using a synthetic water containing 0.06 mg/l of arsenic and 4.8 mg/l of fluoride showed that alumina could lower the arsenic concentration from 0.06 mg/l to around 0.003 mg/l. (Fluoride concentration was also reduced to 1.0 mg/l or less).

Bellack also did column studies on a well water containing more than 0.1 mg/l of naturally occurring arsenic, which showed that arsenic removal was dependent on flow rate and pH of the raw water. The optimum flow rate was established at $1.5–2 \times 10^{-3}$ m/s (2.5–3 gpm/sq ft) and removal increased as the pH decreased from 10 to 7. Under optimum conditions, the initial arsenic content in the effluent was below the detectable limit (0.003 mg/l). The studies also showed that the method of regeneration is significant in maximizing the efficiency of the process.

Because bone char cannot be regenerated for arsenic removal, its use is limited to applications in which it can be discarded when exhausted. Activated alumina can be regenerated and may be economical for arsenic treatment, particularly on waters that are also high in fluoride. The advantages of activated alumina over anion exchange resins include its lower cost and its preference for arsenic in the presence of sulfate and chloride anions.

Until 1977, information on the removal of arsenic with activated alumina was limited to the 1970 laboratory study by Bellack. During 1977, Rubel and Alcoa Laboratories[18] conducted a pilot study on an Arizona groundwater containing about 1.0 mg/l of naturally occurring arsenic, which showed that activated alumina achieved removals below the detectable limit of 0.005 mg/l. Although this information indicates that activated alumina may be a very promising treatment method, pilot-plant studies are recommended before this technique is selected because of the limited amount of laboratory and pilot-plant data and lack of full-scale treatment experience.

Activated carbon. Jar-test studies by Logsdon et al[15] showed that powdered activated carbon (PAC) is not effective for the removal of either arsenic III or V. Less than 3 per cent removals were achieved on water containing 0.5 mg/l of arsenic V with doses of 100-mg/l PAC.† Very poor removals (less than 8 per cent) were obtained with PAC doses up to 300 mg/l on water containing 0.5 mg/l of arsenic III. Studies of the effect of pH in the 6–8.2 range indicated that pH did not affect removal of arsenic III. Based upon the results of these limited studies, powdered activated carbon cannot be considered useful for arsenic removal.

Granular activated carbon (GAC) is very effective for removing organics from water and wastewater. A general review of the technical literature indicates that GAC will also remove some metal salts such as mercury chloride.[19] Because of the widespread interest in GAC for water treatment, the WSRD pilot-plant studies included one or two GAC-filter columns, used in parallel with a dual-media filter, in some test runs (Fig. 6).

The virgin GAC material,* was replaced only occasionally when the plant was shut down for maintenance or repairs. Six months was the longest period that any GAC filter was used, with the usual period being two months. Total organic carbon (TOC) removal was not monitored; thus no data were available to show whether any GAC filters became exhausted because of TOC removal. (None of the virgin GAC was believed to have been exhausted during the arsenic studies, however. Data from other WSRD pilot plant studies showed 40 per cent TOC removal at ten months of continuous treatment of settled coagulated Ohio River water with virgin GAC material.)

Exhausted GAC material was obtained from a full-scale water treatment plant in Virginia. This material was considered to be exhausted for TOC removal for all tests and was generally replaced when the other filter materials were replaced.

The arsenic removal data in Tables 1 and 2 show that, except for test runs 17 and 20 of Table 1, little difference in removal exists between the GAC filters and the dual-media filter, indicating that the GAC did have arsenic adsorption capability. In tests 17 and 20, arsenic removals with the exhausted and virgin GAC media were similar, but both were slightly higher than those achieved by the dual-media filter. The reason suggested for this difference is turbidity removal, not adsorption, because the GAC filters usually had shorter runs and slightly better turbidity removal.

Reverse osmosis and electrodialysis. A general review of the literature including equipment manufacturer information revealed no data on the removal of arsenic from drinking water by either reverse osmosis or electrodialysis. One reverse osmosis equipment specification bulle-

*Alcoa F-1 Alumina, Aluminum Co. of America, Pittsburgh, Pa.

†Nuchar PAC, Westvaco, Covington, Va.

*Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.

Hydrodarco 1030, ICI United States, Inc., Wilmington, Del.

TABLE 3

Results of Conventional Coagulation Pilot-Plant Tests for Selenium Removal

Test No.	Date Started	Length of Test hr	Test Water	Coagulant Type	Coagulant Dose mg/l	pH of Treated Water	Selenium Contaminant Form	Selenium Contaminant Raw Water Concentration mg/l	Percentage Selenium Removed: Settled Water	Filtered Water: Dual-Media Filter	Granular Activated Carbon Filters: Virgin GAC*	Exhausted GAC*	Virgin GAC†
1	5/19/75	100	gravel pit	ferric sulfate	15	6.5	Se IV	0.040	20	58	–	–	–
2	5/26/75	99	gravel pit	ferric sulfate	15	8.5	Se IV	0.050	0	0	–	–	–
3	6/2/75	100	gravel pit	alum	27	8.5	Se IV	0.061	5	8	–	–	–
4	6/9/75	102	gravel pit	alum	20	7.5	Se IV	0.066	23	20	–	–	–
5	6/19/75	100	gravel pit	alum	17	7.5	Se IV	0.050	4	10	–	–	–
6	6/23/75	100	gravel pit	alum	15	6.5	Se IV	0.033	3	6	–	–	–
7	9/20/76	92	Ohio River	ferric sulfate	28	8.3	Se IV	0.017	28	30	41	36	–
8	1/31/77	94	Ohio River	ferric sulfate	25	7.8	Se IV	0.025	64	78	80	80	–
9	2/28/77	100	Ohio River	ferric sulfate	23	6.9	Se IV	0.027	81	81	81	81	–
10	3/7/77	99	Ohio River	ferric sulfate	32	6.5	Se VI	0.097	11	14	23	28	–
11	4/11/77	100	Ohio River	alum	31	6.6	Se IV	0.019	12	20	–	17	17
12	4/25/77	100	Ohio River	alum	30	8.1	Se IV	0.030	28	35	–	30	29
13	5/2/77	100	Ohio River	alum	29	8.1	Se VI	0.076	6	8	–	8	10
14	6/6/77	100	Ohio River	alum	30	8.3	Se IV	0.029	29	20	–	34	27
15	6/13/77	100	Ohio River	alum	30	8.3	Se VI	0.055	0	5	–	20	14
16	7/18/77	82	Ohio River	alum	34	7.9	Se IV	0.022	14	18	–	21	14
17	7/25/77	93	Ohio River	ferric sulfate	29	7.9	Se IV	0.024	47	58	–	63	60
18	9/12/77	91	Ohio River	ferrous sulfate	29	8.1	Se VI	0.042	0	0	–	0	0
19	9/19/77	72	Ohio River	ferrous sulfate	32	8.3	Se VI	0.083	1	2	–	0	5
20	10/31/77	86	Ohio River	alum	25	6.8	Se VI	0.028	18	29	–	0	0
21	1/9/78	76	well water	alum	28	7.6	Se IV	0.056	18	29	–	36	39
22	2/6/78	70	well water	ferric sulfate	33	7.5	Se IV	0.079	69	74	–	74	73
23	2/13/78	90	well water	ferric sulfate	30	8.4	Se IV	0.047	3	79	–	77	77

*Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
†Hydrodarco 1030, ICI United States, Inc., Wilmington, Del.

tin[20] did list an estimated arsenic rejection range of 90–95 per cent. Both treatment methods are very effective for the removal of most dissolved solids and should be effective for arsenic removal.

Arsenic treatment summary. Conventional coagulations using alum or iron can achieve more than 90 per cent removal of environmental levels of arsenic V at pH 7 or below. Above pH 7, iron coagulation can also obtain high arsenic V removal, but alum coagulation removals decrease with increasing pH. Removal can be increased by increasing coagulant dose. Lime softening is also very effective for arsenic V removal, achieving about 100 per cent reductions at pH 10.6 and above. Below this pH level, the removal decreases with decreasing pH. Coagulation and lime softening treatment are poor to moderately effective for the removal of arsenic III. Iron coagulation can achieve 50–60 per cent removal in the normal pH operating range. Lime softening removals are pH dependent, with best removals (70–80 per cent) occurring above pH 11. Below pH 11, removal decreases with decreasing pH to as low as 15–20 per cent at pH 10.2. The least effective method for arsenic III removal is alum coagulation with removal below 20 per cent achieved throughout the common operating pH range.

Arsenic III removals identical to those of arsenic V can be achieved by conventional coagulation and lime softening if the arsenic III is oxidized to arsenic V prior to treatment. Chlorine and potassium permanganate easily oxidize arsenic III to arsenic V whereas aeration was not found effective. Ozone and other strong oxidants should also be successful. Preoxidation with chlorine may not be always advisable because of the potential formation of chloroform and other trihalomethanes by the reaction of chlorine with organic material in the water. This potential should be investigated thoroughly before a preoxidation step is chosen and an oxidant selected, because the solution to one problem could create a more serious one.

Ion exchange treatment using an anion exchange resin, activated alumina, or bone char can remove both forms of arsenic. Little information is available, however, on the competitive effect of other anions on the efficiency of these materials. Bone char cannot be regenerated and therefore would have application only on a throw-away basis. Pilot-plant studies conducted on the actual water to be treated would be an absolute necessity prior to the design of an ion exchange plant.

Because reverse osmosis and electrodialysis are very effective in the removal of most dissolved solids, both treatment methods should also be effective for arsenic removal.

The WSRD research plan for fiscal year 1978 for the removal of arsenic is to study the effectiveness of reverse osmosis and ion exchange with activated alumina. The Charlotte Harbor, Fla., reverse osmosis project, described in the nitrate removal section of Part 1, will provide reverse osmosis rejection data for various arsenic concentrations in natural waters. Laboratory studies on the removal of arsenic from water by reverse osmosis and activated alumina will also continue at the EPA Envir. Res. Ctr. in Cincinnati, Ohio.

Selenium Removal From Water

Health effects. Prior to 1962, the USPHS limit for selenium in drinking water that constituted grounds for rejecting a water supply was 0.05 mg/l. Because of concern over the possible carcinogenic properties of selenium, the USPHS lowered the limit to 0.01 mg/l in the 1962 revised PHS standards. The limit was maintained by EPA in establishing the 1976 NIPDWR. Controversy continues to exist over the MCL for selenium because data supporting carcinogenicity has not been forthcoming or confirmed in prop-

erly conducted studies. Moreover, selenium is considered an essential nutrient and some evidence suggests that it may provide some protection against certain types of cancer.[2] On the other hand, chronic exposure to excess selenium results in dermatitis and central nervous system and gastrointestinal disturbances, and very large doses can cause death.[2] Selenium, therefore, is similar to fluoride and some other elements, in that it has both adverse and beneficial effects depending on the amount ingested. Some studies also indicate that the beneficial or adverse effects of selenium are dependent on the mode of intake, the form of selenium, the presence of other trace metals, and other factors.[1]

The EPA supporting background information for the NIPDWR states that the 0.01-mg/l limit provides a safety factor of about three, considering the lower end of the range of selenium intakes associated with minor toxic effects in man.[1] This factor was based upon an estimated average selenium intake of an American person as 200 μg/day from sources other than water, and on the assumption that an individual consumes 2 l of water per day. The National Academy of Science (NAS) report[2] on the NIPDWR draws no firm conclusion on the adequacy of the selenium MCL. It does state, however, that "most evidence indicates that there is a greater overall potential for selenium deficiency than for selenium toxicity at current levels of selenium intake." The report further states that "the no-observed-adverse-health effect level for selenium in water is at least 100 μg/l and appears to be as great as 500 μg/l." NAS recommended a nine-point research program that included studies on developing baseline data on selenium levels in humans in health and disease.

Chemistry overview. Selenium is similar to arsenic in several ways. Selenium has several oxidation states, but only two are predominant in water: selenium IV (selenite) and selenium VI (selenate). Like arsenic, selenium occurs as an anion in water and thus has acid characteristics.

Selenous acid, H_2SeO_3, is a weak acid that dissociates in water into two selenite species, $HSeO_3^-$ and SeO_3^{-2}. The concentration of each is dependent on the pH of the water, with SeO_3^{-2} predominant at pH 7.[21]

Selenic acid, H_2SeO_4, is a strong acid that forms only one species in water, SeO_4^{-2}. The solubility of most salts of selenic acid are similar to those for the sulfates of the same metals. Most selenate salts are more soluble than the corresponding selenite salts.[21]

Several geochemical studies of selenium in natural soils and waters[22-28] are helpful in explaining the results of chemical coagulation studies on the removability of selenite and selenate from drinking water. One study showed that selenium VI is taken up easily by plants whereas selenium IV is not.[26] The explanation for the phenomenon is that selenium IV is fixed in the soil as a result of its precipitation with natural ferric hydroxide, and to some extent with other metal hydroxides such as aluminum hydroxide. Plotnikov[22-24] and Olson and Jensen[28] conducted several studies on the coprecipitation of selenium with ferric hydroxide and found that selenium IV is more readily removed than selenium VI. The use of ferric hydroxide precipitation was even suggested as a method to separate the two selenium forms.[22] Plotnikov's in-depth investigations revealed that selenium removal is probably a combination of coprecipitation and adsorption that is dependent on various factors such as pH, selenium concentration, and the amount of ferric hydroxide. Plotnikov also showed that ferric hydroxide was more effective than aluminum hydroxide in removing selenium.

Hingston,[25] in studying the effect of pH on selenium IV removal, showed that a maximum amount of adsorption occurs at any one pH and that this amount decreases with increasing pH. Howard[27] compared the use of two types of clays to ferric hydroxide and found that ferric hydroxide was much more effective than the clays for selenium IV removal.

Another significant finding of selenium chemistry that has application to its removal from water is that the transformation of selenite to selenate is very slow, and that both forms in the same solution are very stable.[22,26] Neither form can be oxidized easily or reduced to its other valence state. These studies indicate that conventional coagulation treatment should remove selenium IV much more effectively than selenium VI and that removals are dependent on various operating conditions.

Data from the 1969 Community Water Supply[3] study showed that only 16 of 952 finished water samples exceeded the 0.01-mg/l selenium limit. The maximum level reported was 0.065 mg/l; the minimum level was 0.002 mg/l, and the mean 0.003 mg/l. Thus there were very few selenium problems in the finished water of the treatment systems studied.

Little information is available by which to estimate the magnitude of the selenium problem. Because selenium is not a common industrial pollutant, it is

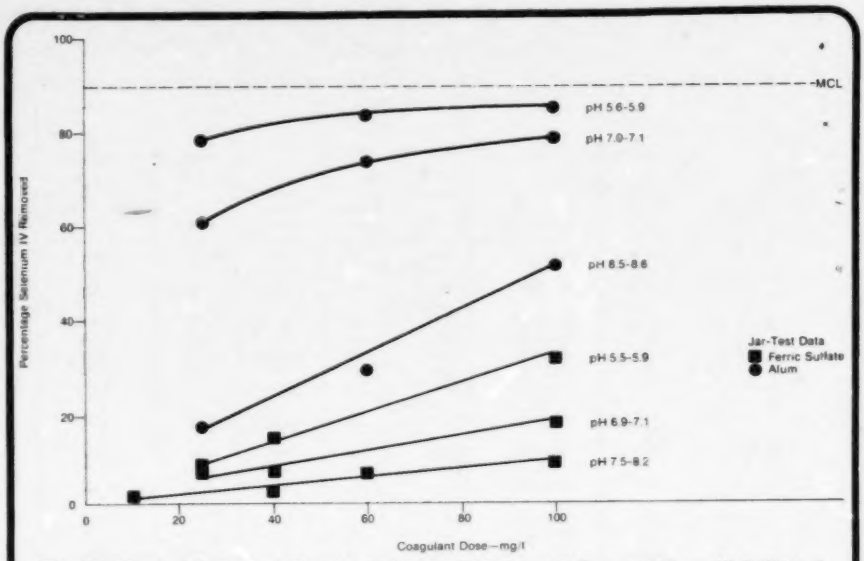


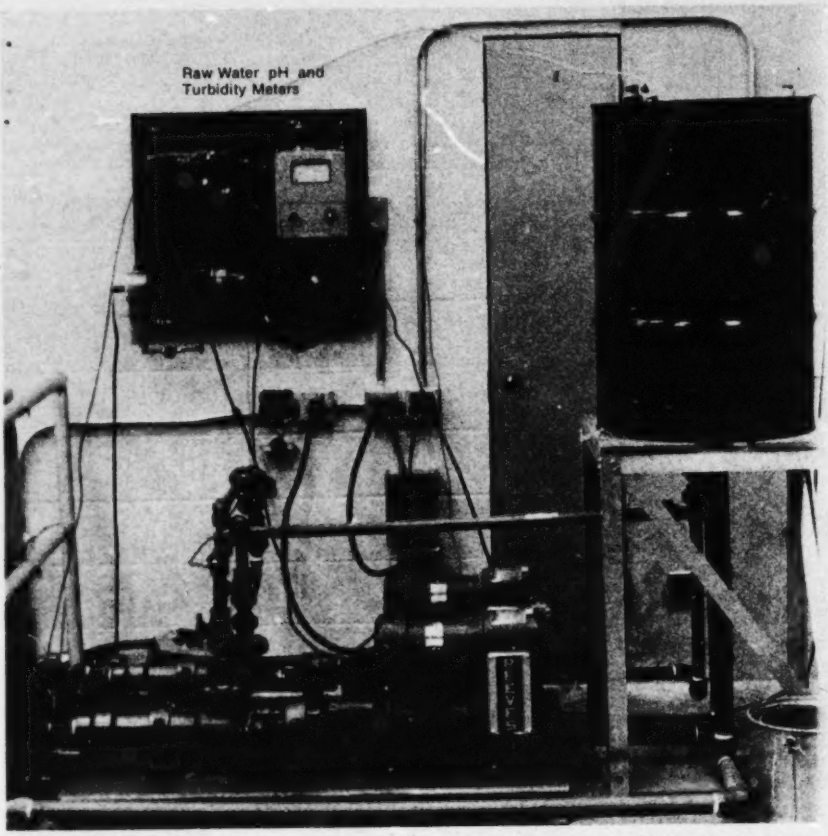
Fig. 10. Effect of Coagulant Dose on Selenium IV (0.1 mg/l) Removal From Well Water[15]

TABLE 4

Results of Lime Softening Pilot-Plant Tests for Selenium Removal from Well Water

Test No.	Date Started	Length of Test hrs	pH of Treated Water	Selenium Contaminant		Percentage Selenium Removed			
						Settled Water		Filtered Water	
				Form	Raw Water Concentration mg/l	First Stage	Second Stage	Dual-Media	GAC*
1	3/3/75	59	9.5	Se IV	0.038	21	—	30	34
2	3/24/75	99	11.3	Se IV	0.028	38	46	46	46
3	3/31/75	95	11.3	Se VI	0.038	16	3	8	8
4	4/7/75	101	9.5	Se VI	0.038	11	—	3	0

*Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.



Raw waters for arsenic and selenium removal studies included Cincinnati tap water, gravel pit water, Ohio River water, and well water. Shown here are a raw water pump, and raw water pH and turbidity instrumentation.

more likely to be found in groundwaters than in surface waters. Several surveys have shown that selenium problems may be numerous in certain localities. Engberg[29] reported that the 0.01-mg/l selenium limit was exceeded in 40.3 per cent of 139 groundwaters surveyed in Nebraska. The two highest concentrations were 0.48 mg/l and 0.103 mg/l. Thirty-nine surface waters were also sampled and 25 per cent of these had maximum levels of more than 0.01 mg/l. The highest level reported was 0.02 mg/l, twice the MCL. Selenium is associated with uranium mining and has been reported in groundwaters in mining areas of Colorado, Arizona, and New Mexico. An EPA study[30] of the water quality in the Grants Mineral Belt, N.M., showed selenium levels of 0.05 to 0.11 mg/l in industry potable water supplies.

Studies on the occurrence of selenium in ground- and surface waters have reported results as total selenium and have not identified the specific species found. For general monitoring purposes, total selenium concentration measurements are certainly sufficient. However, because the effectiveness of certain treatment techniques, such as lime softening and conventional coagulation, depends on the oxidation state of the selenium, identification of the oxidation state may be necessary before a selection of treatment. No simplified analytical techniques to identify the form of selenium presently exist. However, ferric hydroxide precipitation of selenium IV has been suggested to separate selenium IV from selenium VI. In lieu of more refined analytical techniques, a standard jar test using an iron coagulant in the pH range 6–7 could determine the valence of selenium in raw water. If the iron coagulant lowers the selenium level of the raw water significantly, selenium IV is present. If the raw water contains a mixture of the two valence forms, the technique will be less useful.

Treatment methods. Very little work has been done on removing selenium from drinking water. The only in-depth studies have been conducted by the WSRD, and were reported in part by Logsdon et al[15] and Sorg and Logsdon.[31] These studies were primarily coagulation and lime softening laboratory jar-test studies. Since these reports were published, pilot-plant studies have been done and are described here.

A review of the wastewater treatment literature showed a number of studies done on the removal of trace metals from wastewater, but rarely was selenium included among the list of contaminants. The most pertinent wastewater studies were reported by Hannah and Cohen[32] and Linstedt et al.[33]

Conventional coagulation. Jar tests and pilot-plant tests conducted by the WSRD on the removal of selenium from ground- and surface waters by conventional coagulation showed that selenium removal is dependent on the oxidation state and the initial concentration of selenium, the pH of the treated water, and the type and doses of coagulant. Under optimum operating conditions, the highest removals of selenium IV were about 80 per cent. This treatment technique was ineffective for removing selenium VI, with 10 per cent or less removal obtained. These studies were done primarily with well water because it was assumed that the low valence selenium IV is more likely to be found in groundwater. Because the literature indicated the selenium IV may also be found in surface waters, several tests were conducted with Ohio River water. Alum and ferric sulfate were used as coagulants and the selenium concentrations ranged from 0.03 to near 0.1 mg/l. The results are shown in Fig. 9. The removal curves indicate that ferric sulfate achieved much higher selenium IV removals than alum, and that ferric sulfate coagulation removals are pH dependent. The highest removals (70–80 per cent) were achieved with iron coagulation in the 6–7 pH range with Ohio River water. Removals decreased with increasing pH to a minimum near 10 per cent at pH 9. When the tests were repeated using a low turbidity groundwater, selenium IV removals were slightly less, but the same decreasing trend was observed. Alum coagulation removals of selenium IV were significantly less (20 per cent) than those of iron coagulation with both types of water. Moreover, the pH had little effect on removals with the 25-mg/l dose used in the experiments.

If higher selenium IV removals are required, removals can be increased by using larger coagulant doses (Fig. 10). The improvements achieved by increasing the iron dose at low pH are smaller than those for pH 8.5 and above, which is expected because initial removals with low doses of coagulant are much higher in the low pH range. Conversely, alum coagulation produced greater overall increases in removals in the lower pH range, even though there was little pH dependency.

The jar-test studies with selenium VI showed less than 10 per cent removal by both ferric sulfate and alum coagulation through the pH range 6–8. When larger coagulant doses were used, no signifi-

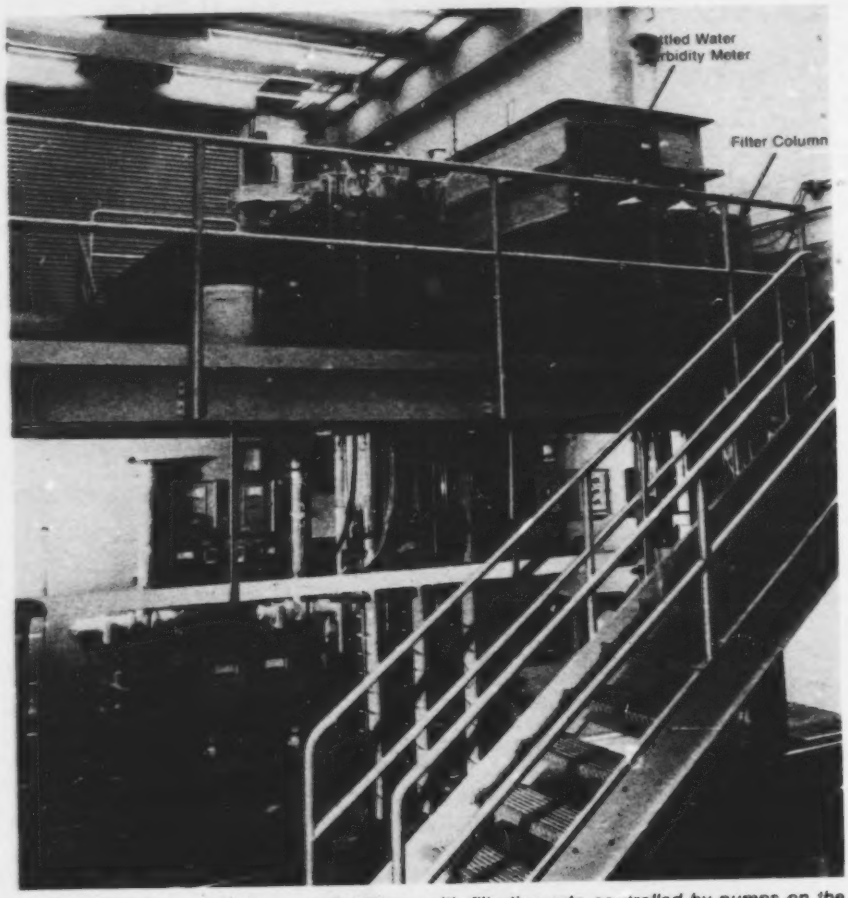
cant increases in removals were obtained with either coagulant.

A dose of 25–30 mg/l of ferric sulfate can achieve the selenium MCL when the selenium IV concentration in groundwater is 0.03 mg/l or less and the pH of the treated water is less than seven (Fig. 9). To determine the effect of higher concentrations of selenium IV, jar tests were conducted with selenium concentrations to 5.0 mg/l. The results of these tests, using 25 mg/l of alum and ferric sulfate at pH 7.7 and 7.2 respectively, are shown in Fig. 11. With coagulant doses in the range commonly used for turbidity removal in surface waters, alum coagulation is able to achieve the MCL on groundwater containing selenium IV concentrations only slightly above the MCL. Similar doses of ferric sulfate are capable of lowering the selenium IV level to the MCL only if the initial selenium concentration is two times the MCL. These data clearly illustrate that even ferric sulfate coagulation is not a practical method for removing selenium IV from groundwater unless the initial concentration is only slightly above the MCL. For selenium IV concentrations of 0.02 mg/l and above, larger coagulant doses and pH adjustment would be required.

Following completion of the jar-test experiments, the WSRD ran pilot-plant studies with the system shown in Fig. 6. Alum and ferric sulfate coagulation tests done with the variety of spiked test waters used in the arsenic tests produced the results shown in Table 3. The dual-media filter removal results are also plotted on Fig. 9 for comparison to the jar-test study results.

The pilot-plant results were almost identical to those from jar-test studies. Ferric sulfate and alum coagulation achieved less than 10 per cent removal of selenium VI. Selenium IV removals varied from near zero to about 70 per cent depending on the coagulant used and the pH of the water. The pilot-plant results confirmed the conclusion drawn from the jar-test studies—that although ferric sulfate is much more effective than alum, even ferric sulfate coagulation is not a very good treatment method for removing selenium IV.

Lime softening. Jar-test and pilot-plant studies on the removal of selenium by lime softening showed that this treatment technique is not very effective for the removal of either selenium IV or selenium VI. Selenium VI removals were similar to those of conventional coagulation treatment: less than 10 per cent removal through the pH range 9.0–11.5. Removals of selenium IV were only slightly higher (Fig. 12). The maximum removal, obtained with the hard well water spiked with 0.1 mg/l selenium IV, was about 50 per cent at pH 11.5. Below this pH, removals decreased with decreasing pH. With only 0.03 mg/l of selenium IV, the percentage of removals was about the same.



Each treatment train has four parallel filters, with filtration rate controlled by pumps on the effluent side of each filter. Shown here are filter columns and filtered water pH and turbidity instrumentation.

Pilot-plant tests were conducted on the removal of selenium IV at pH 9.5 and 11.3 with the same well water used in the jar-test studies. The results are given in Table 4 and the dual-media filter results are plotted in Fig. 12. Although the pilot-plant results were slightly higher than those in jar-test studies, they were not significantly higher, indicating that lime softening is not a good method for selenium removal.

Ion exchange. Because conventional coagulation and lime softening are ineffective for selenium VI removal and only moderately effective for selenium IV removal, the WSRD investigated the use of ion exchange. Column tests were run using distilled water spiked with 0.1 mg/l of either selenium IV or VI. Six litres of the test solution were passed through two ion-exchange columns in series. The first column contained a cation resin* and the second one, an anion resin.* Samples of the effluent from the anion column were collected at 2, 3, 5, and 6 l. Only one sample was collected from the cation resin column, at the 3-l point. For all samples 12.5 per cent removal of selenium IV was effected by the cation resin and more than 98 per cent by the two resins in series. The selenium VI test results were almost identical to those of selenium IV. The cation effluent sample showed a 7.4 per cent removal; cumulative removals by both resins were above 98 per cent for all samples. Because selenium occurs as an anion, the low removal in the cation column was expected.

In a study by Linstedt et al[33] investigating the ion exchange process for selenium IV removal as part of a wastewater pilot-plant study, the results were similar to the WSRD results with distilled water. A cation ion exchange resin removed only 0.9 per cent, whereas cation and anion resins in series removed over 99 per cent. In these tests, essentially all of the selenium IV removal occurred in the anion exchange resin column.

Although the two ion exchange studies reported upon were very limited, they

*IR-120, IRA-458, Rohm & Haas, Philadelphia, Pa.

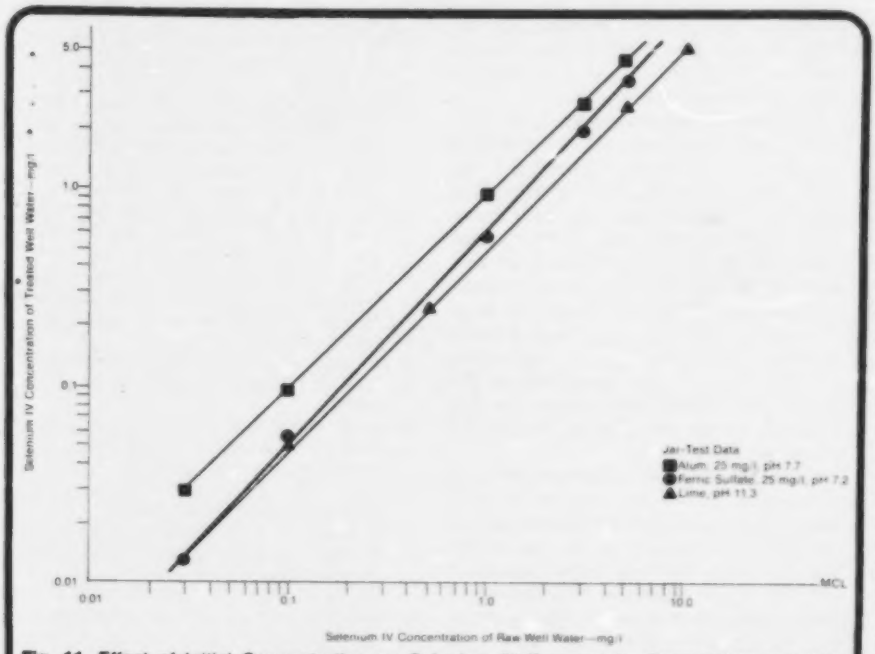


Fig. 11. Effect of Initial Concentration on Selenium IV Removal by Coagulation and Lime Softening Treatments[31]

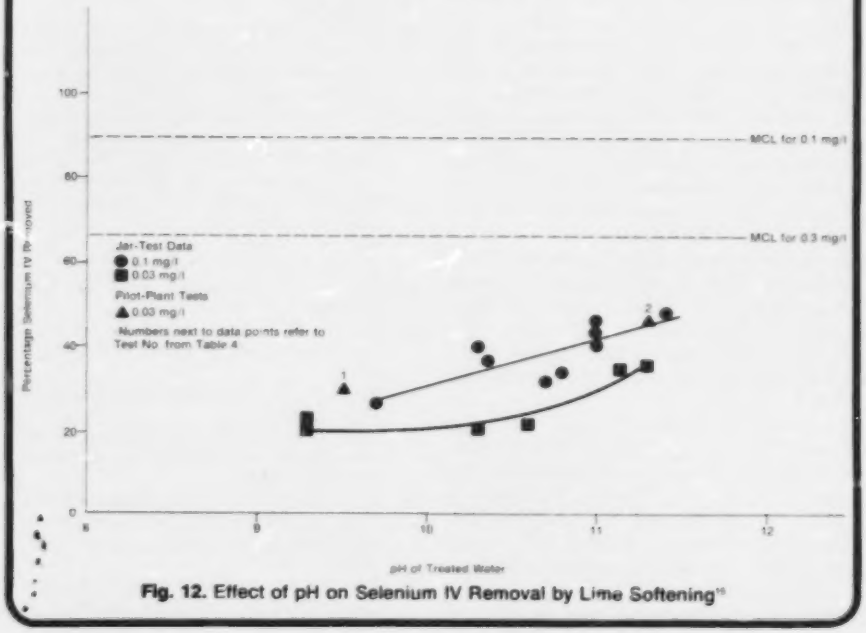


Fig. 12. Effect of pH on Selenium IV Removal by Lime Softening[15]

indicate that both valence forms of selenium can be removed from water and wastewater by anion exchange resins. Research on both laboratory and pilot-plant scale is needed before the feasibility of this treatment technique for full-scale use can be determined.

Because activated alumina has been shown to remove arsenic from water, and because of the similarities between arsenic and selenium, the WSRD recently began to investigate activated alumina for selenium removal, using column tests with activated alumina.* Separate experiments were conducted for the removal of selenium IV and VI with distilled water and a hard groundwater from Wyoming, Ohio. The studies with spiked distilled water (0.3 mg/l) showed very high removals (95 per cent and above) of both selenium IV and VI. When the experiments were repeated with the groundwater with total dissolved solids (TDS) of 608 mg/l, however, selenium IV removals ranged from 62–88 per cent and essentially no selenium VI was removed.[34] The initial reason proposed for the decreased removal was the valence of the anion species. At the pH of the test waters (6.8–7.0), however, the predominant species of both selenium IV and VI are divalent anions SeO_3^{-2} (Se IV) and SeO_4^{-2} (Se VI). Furthermore, the anion selectivity series of alumina reported by Kubli[35] indicates that activated alumina does not show a strong preference for monovalent over divalent anions (see Part 1, Fluoride Removal). This selectivity series does show that alumina has a low preference for sulfate, SO_4^{-2}, and a rather high preference for sulfite, SO_3^{-2}. The literature indicates that selenate is similar to sulfate; if selenite is chemically similar to sulfite, this would explain the difference in removals of selenium IV and VI by activated alumina.

The activated alumina studies for fluoride and arsenic removals discussed in prior sections of this article indicated that removals are dependent on the pH of the influent water, flow rate, and regeneration procedures. Most of the selenium experiments were conducted under the same conditions and procedures. Several test runs were made at different flow rates and pHs, but because of the small number of experiments the data were insufficient to evaluate the effect of these variables on selenium IV and VI removal. The only conclusion that can be drawn at this time is that activated alumina may be effective for selenium IV removal and ineffective for selenium VI removal. Further research is required to evaluate the variables that affect selenium removal and to determine operating conditions to optimize removal. If selenium removal is ultimately found to be valence dependent, this would be a shortcoming in the use of activated alumina.

Activated carbon. The WSRD conducted jar-test studies to determine the removal of selenium IV and VI from water by powdered activated carbon (PAC), which showed that less than 4 per cent of either selenium species could be removed with PAC doses up to 100 mg/l on well water spiked with selenium concentrations of 0.03 and 0.1 mg/l. Tests done at several pH values showed that pH had no effect on removals.

In jar tests done by Thiem and O'Connor[36] with three different types of PAC on the removal of 0.05 mg/l of selenium IV at pH 7, 8, and 9, the results were almost identical to the results of the WSRD, with 4 per cent or less removal achieved with doses up to 100 mg/l. The lack of effectiveness of PAC is not surprising, because PAC is noted for its ability to remove organics and not inor-

*Alcoa F-1 Alumina, Aluminum Co. of America, Pittsburgh, Pa.

ganics. Furthermore, activated carbon has a net negative surface charge. Because selenium occurs as an anion and therefore has the same charge as the activated carbon, adsorption onto activated carbon would not be expected.

The WSRD pilot plant results shown in Tables 3 and 4 indicate that granular activated carbon (GAC) does not adsorb selenium. The selenium removals of the GAC filters are almost identical to those of the dual-media filter. The removal mechanism of the GAC filters is therefore attributed entirely to turbidity removal.

Hannah et al[32] and Linstedt et al[33] conducted pilot-plant studies for the removal of selenium IV and other metals from wastewater. The pilot-plant system consisted of advance wastewater treatment processes that included GAC filters following either sand or dual-media filters. Although removals were extremely variable, several test runs achieved substantial increases in removals of selenium IV by the GAC filters. The variability in the wastewater results, and the differences in removals between the water supply and wastewater studies, may be explained by the high organic content of the wastewater in contrast to the low organic levels in the well and gravel pit waters used in the water supply studies. Some organic-selenium complexes might have been formed in the wastewater studies that resulted in higher selenium removal by the GAC.

Reverse osmosis and electrodialysis. The WSRD conducted two brief experiments to determine selenium removal by reverse osmosis (RO). The RO system was a small portable unit containing a cellulose acetate membrane. During a 60-min test run with Cincinnati tap water (360 mg/l TDS) spiked with 0.1 mg/l of selenium IV, seven product water samples showed selenium removals above 97 per cent. The RO operating pressure was 1350 kPa (190 psi), the flow rate was 1.3 l/min, and the pH of the water was 7.3. For the selenium VI experiments on Cincinnati tap water spiked with 0.1 mg/l of selenium VI, the TDS content was raised to almost 3000 mg/l with sodium chloride and calcium sulfate. The RO flow rate was 1.5 l/min, the operating pressure was 1295 kPa (185 psi), and the raw water pH was 6.3. Fifteen samples collected during a 140-min test run all had selenium VI removals above 97 per cent. A general review of the literature did not reveal any other test data for selenium removal by reverse osmosis, but one equipment manufacturer estimated the removal range of selenium at 90–95 per cent.[29] Because reverse osmosis is effective for the removal of most dissolved substances, it should also have high rejection capability for selenium.

No information was found on the removal of either selenium IV or VI by electrodialysis. Electrodialysis, like reverse osmosis, has good rejection characteristics for most ions and should be effective for selenium removal.

Selenium treatment summary. Lime softening and conventional coagulation treatment with either alum or iron coagulants are ineffective for removing selenium VI from water. The only treatment methods that can achieve high removals (90 per cent or above) of selenium VI are ion exchange, reverse osmosis, and electrodialysis. None of these techniques, however, has been demonstrated on either a small or large scale, and little research has been done on the proper operational procedures for ion exchange or on the effect of competing anions on this process.

Moderate removals of 40–80 per cent of selenium IV can be achieved by iron coagulation treatment. The percentage of removal is dependent on the pH of the treated water, the iron coagulant dose, and the initial selenium concentration. Alum coagulation is not a good method for selenium IV removal; only 15–20 per cent removal can be obtained with alum doses of 20–30 mg/l. The effectiveness of lime softening for selenium IV removal lies between that of iron and alum coagulation. Lime softening removals are pH dependent but even at optimum pH, removals are only 35–45 per cent.

The most effective treatment methods for selenium IV removals are the same as those given for selenium VI removal: ion exchange, reverse osmosis, and electrodialysis. None of these has been demonstrated on even a pilot scale.

Preliminary studies on the removal of selenium by activated alumina indicate that it may be a good method for selenium IV removal and a poor method for selenium VI removal. Because of insufficient data, however, no firm conclusion can be drawn.

The WSRD research plan for fiscal year 1978 for selenium removal is to continue in-house investigations on the use of activated alumina and reverse osmosis. The reverse osmosis research project in Charlotte Harbor, Fla., mentioned in previous summary sections, will also include the evaluation of selenium IV and VI removal by low and high pressure RO systems. A pilot-plant study on the removal of naturally occurring selenium from well water by activated alumina is also planned.

References

1. National Interim Primary Drinking Water Regulations. EPA-570/9-76-003, Ofce. of Wtr. Sply. Washington, D.C. (1976).
2. Drinking Water and Health, Recommendations of the National Academy of Science. *Fed. Reg.* 42:132:35764 (Jul. 11, 1977).
3. McCabe, L.J. et al. Survey of Community Water Supply Systems. *Jour. AWWA*, 62:11:670 (Nov. 1970).
4. Kopp, J.F. & Kroner, R.C. *Trace Metals in the Water of the United States*. Fed. Wtr. Qual. Admin. Cincinnati, Ohio (1970).
5. Durham, W.H.; Hem, J.D.; & Heidel, S.G. Reconnaissance of Selected Minor Elements in Surface Waters of the United States. Geol. Surv. Cir. 643, US Dept. Interior, Washington, D.C. (1970).
6. Ferguson, J.F. & Gavis, J.A. Review of the Arsenic Cycle in Natural Waters. *Wtr. Res.* 6:11:1259 (Nov. 1972).
7. LaPeintre, M. Solubilization par les eaux, Naturelles de l'arsenic lie au fer dans les Roches Sedimentaires. *C.R. Acad. Sci.*, 239:359 (1954).
8. Osishi, H. & Sanell, E.B. Geochemistry of Arsenic. *Geochim. Cosmochim. Acta.*, 7:1 (1955).
9. Mackenthun, K.M. Aquatic Weed Control with Sodium Arsenite. *Sew. and Ind. Wastes*, 22:8:1062 (Aug. 1950).
10. Frear, O.E. *Agricultural Chemistry*, 2:532, Van Nostrand, Toronto (1952).
11. Gilderhus, P.A. Some Effects of Sublethal Concentrations of Sodium Arsenite on Bluegills and the Aquatic Environment. *Trans. Am. Fish. Soc.* 95:289 (1966).
12. Buswell, A.M. et al. War Problems in Analysis and Treatment. *Jour. AWWA* 35:10:1303 (Oct. 1943).
13. Shen, Y.S. Study of Arsenic Removal from Drinking Water. *Jour. AWWA*, 65:8:543 (Aug. 1973).
14. Gulledge, J.H. & O'Connor, J.T. Removal of As(V) from Water by Adsorption on Aluminum and Ferric Hydroxide. *Jour. AWWA*, 65:8:548 (Aug. 1973).
15. Logsdon, G.S.; Sorg, T.J.; & Symons, J.M. Removal of Heavy Metals by Conventional Treatment. *Proc. 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance and Control*. Univ. Bull. No. 71. Univ. of Illinois, College of Engrg., Urbana-Champaign, Ill. (1974) p. 111.
16. Calmon, C. Comments. *Jour AWWA*, 65:8:586 (Aug. 1973).
17. Bellack, E. Arsenic Removal from Potable Water. *Jour. AWWA*, 63:7:454 (Jul. 1971).
18. Rubel, F. Jr. Personal Communication (Jan. 31, 1978).
19. Symposium on Activated Carbon D-114. Atlas Chem., ICI America Inc. Wilmington, Del. (1972).
20. Pure Drinking Water, Polymetrics Reverse Osmosis Equipment. Pull. 950—Rev. 1, Polymetrics, Inc. Santa Clara, Calif. (1974).
21. Selenium. *Medical and Biologic Effects of Environmental Pollutants Series*. Nat. Res. Council, Nat. Acad. of Sciences, Washington, D.C. (1976).
22. Plotnikov, V.I. Coprecipitation of Small Quantities of Selenium. *Zhur. Neorg. Khim.*, 3:8:1761 (1958).
23. Plotnikov, V.I. Coprecipitation of Selenium and Tellurium with Metal Hydroxides. *Russ. J Inorg. Chem.*, 5:3:351 (Mar. 1960).
24. Plotnikov, V.I. Coprecipitation of Small Amounts of Selenium and Zinc with Metal Hydroxides. *Russion Jour.-of-Inorg. Chem.* 9:2:245 (Feb. 1964).
25. Hingston, F.J.; Posner, A.M.; & Quirk, J.P. Adsorption of Selenite by Geothite. *Advances in Chemistry Series* 79:82 (1968).

26. Geering, H.R. et al. Solubility and Redox Criteria for the Possible Forms of Selenium in Soils. *Soil Sci. Soc. Amer. Proc.* 32:35 (1968).
27. Howard, J. Hatten III. Control of Geochemical Behavior of Selenium in Natural Waters by Adsorption on Hydrous Ferric Oxides. *Trace Substances in Environmental Health–V.* (D.D. Hemphill, editor). Univ. of Missouri, Columbia (1972).
28. Olson, O.E. & Jensen, C.W. The Absorption of Selinate and Selenite Selenium by Colloidal Ferric Hydroxide. *Proc. S. Dak. Acad. Sci.* 115:21 (1940).
29. Engbery, R.A. Selenium in Nebraska's Groundwater and Streams. Neb. Wtr. Surv. Paper No. 35. Univ. of Nebraska, Conservation and Surv. Div., Lincoln, Nebraska (Dec. 1973).
30. Impact of Uranium Mining and Milling on Water Quality in the Grants Mineral Belt, New Mexico. USEPA, Region VI, Dallas, Tex., EPA 906/9-75-002 (Sep. 1975).
31. Sorg, T.J. & Logsdon, G.S. Removal of Selenium from Water–State of the Art. *Proc. Symposium on Selenium-Tellurium in the Environment.* Industr. Health Foundation, Inc. Pittsburgh, Pa. (May 1976).
32. Hannah, S.A.; Jellus M.; & Cohen, J.M. Removal of Uncommon Trace Metals by Physical and Chemical Treatment Processes. *Jour. WPCF.* 49:11:2297 (Nov. 1977).
33. Linstedt, K.D.; Houch, C.P.; & O'Connor, J.T. Trace Element Removals in Advanced Wastewater Treatment Processes. *Jour. WPCF.* 43:7:1507 (Jul. 1971).
34. Ball, R. Removal of Selenium from Drinking Water Using Activated Alumina. Unpublished senior thesis. Dept. of Civ. Engrg., Univ. of Cincinnati, Cincinnati, Ohio (Sep. 1977).
35. Kubli, H.A. Contribution to the Knowledge on Anion Separation by Means of Adsorption on Alumina. *Helv. Chem. Acta.*, Switzerland 3:453 (1947).
36. Thiem, L. & Connor, J.F. Removal of Barium, Cadmium, Mercury, and Selenium from Drinking Water Supplies. Dept. of Civ. Engrg., Univ. of Missouri, Columbia, Mo. (1977).

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